

MODEL OF LINKS STORAGE CREATED BETWEEN NANOTUBES BY IRRADIATION

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Introduction

Particles beams are a unique tool of delivery of energy, momentum, charge and mass into a nanostructure. Investigations of their interaction with nanotubes can be conventionally divided into two groups: 1) researches of a collision lasted up to interaction between partners is switching off [1-3]; 2) researches of the nanostructure relaxation after that which can last longer on several orders and give a new equilibrium state with a defect, partial or complete fragmentation of structure [4-7]. A state of nanostructure at once after collision can be estimated approximately by traditional methods [8] at least as a first approximation, despite of some discrepancy with traditional representations about nuclear and electronic energy losses [2,3]. The neighbors of the shocked area essentially influence on the relaxation processes therefore palette of final outcomes is richer here. Authors [4] have used MD to simulate ion bombardment of crossed nanotubes to join them and demonstrated that ion irradiation should result in welding of them, both suspended and deposited on substrates. In [5] it has been shown experimentally that ion beam selectively removes nanotubes lying on substrate and suspended between pillars of Si/SiO₂ structures, leaving the suspended nanotubes in place but destroying the laying ones. In [6] it has been shown experimentally that ion irradiation can create molecular junctions between crossed single-wall carbon nanotubes as well as between walls inside a multiwalled nanotube. Authors [7] have introduced stable links between neighboring carbon nanotubes within bundles, using moderate electron-beam irradiation inside a TEM. They have assumed that crosslinking is most probably not due to a local change in atom hybridization only, because of a prohibitively large intertube distance. They have shown that crosslinks can form with the participation of interstitial atoms created by beam, or by a radiation-induced chemical reaction between carboxyl groups, which requires the

simultaneous presence of two chemical groups on opposing nanotubes and is much less probable.

Model and methods

The purpose of this work is to model storage dynamics of the crosslinkings between nanotubes or theirs inner walls under particle beams radiation, taking into account different mechanisms of the bonds creation. We focus our attention on change of an amount of the links between nanotubes (suspended between pillars, deposited on substrate, linked with each other within bundles and so on) due to variation of particles dose and energy.

A particle (electron/ion) with energy E creates a cascade of excited carbon atoms and possibly radiation defects inside of a target containing nanotubes and some impurities (interstitial carbon, carboxyl groups). Hence, necessary conditions can appear to creation of the crosslinkings by several mechanisms: *i*) cycloaddition reaction [9]; *ii*) radiation defects; *iii*) impurities group [7].

The specific concentrations of carbon atoms in nanotubes, participating in the crosslinkings by i -th mechanism, we denote by $C_i(\Phi)$, and the same for agent (excited tube's atom, interstitial atom, impurities group), launched and stimulated this mechanism, we denote by $A_i(\Phi)$. Then we can use general equations of chemical kinetics:

$$\begin{aligned}\frac{dA_i(\Phi)}{d\Phi} &= (1 - N_{g,i})\sigma_i - \sum_{k=1}^3 \frac{1}{j\tau_k} p_{i,k}(C) A_k, \\ \frac{dC_i(\Phi)}{d\Phi} &= \sum_{k=1}^3 \frac{1}{j\tau_k} p_{i,k}(C) A_k - \sum_{j=1}^3 m_{i,k} C_k \sigma_k, \quad (1) \\ N_{g,i} &= \sum_{k=1}^3 (l_{i,k} A_k + m_{i,k} C_k), \quad i = 1 \dots 3,\end{aligned}$$

where $\Phi = jt$ is an irradiation dose, j is a density of particles current, t is the irradiation time, $\sigma_{i,k}$ are effective total cross sections of the A_i and C_k generation, τ_k are lifetimes for different processes,

$p_{i,k}$, $l_{i,k}$, $m_{i,k}$ are coefficients depending on geometry of process and its participants. The cross sections depend on the particle's energy, and all above designating are dimensionless.

Despite of awkwardness (1), they contain no more than twenty coefficients which we have calculated, estimated, or found from experiments [7,10]. Therefore its solutions can display, at least in general, the behavior of the crosslinkings amount created during beam irradiation.

Results and discussion

Solution of system (1), in the simplest cases when it becomes linear, can be found analytically at the initial conditions: $C_i(0) = A_i(0) = 0$, $i = 1..3$,

$$C_i(\Phi) \approx \frac{1}{1-\beta} (e^{-\sigma\beta\Phi} - e^{-\sigma\Phi}), \quad (2)$$

$$A_i(\Phi) \approx A_{i,\infty} - \delta e^{-\sigma\beta\Phi} + \lambda e^{-\sigma\Phi},$$

where σ , β , δ , γ are some constants depending on the above parameters. Typical curves are presented on the Fig.1 for reaction of cycloaddition that is $i=1$. We used effective cross section calculated in [11], and other parameters were estimated by us too.

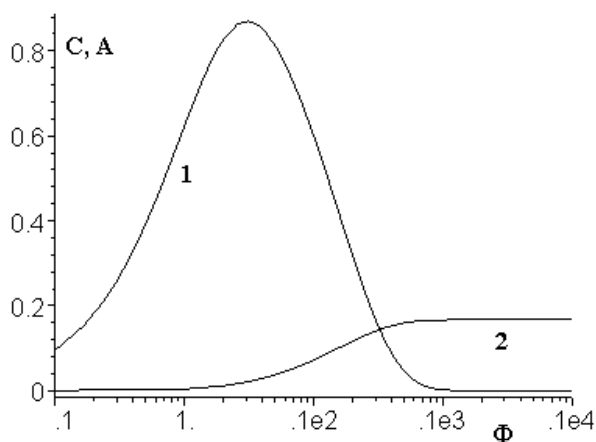


Fig.1. Dose dependence of C_1 , A_1 (curves 1 and 2, respectively) at electron irradiation of fullerite C_{60} with $E=1$ keV.

In approach of low specific concentrations we investigated a linear approach of (1) and have found arrays of parameters' values where its solution has the characteristic view presented on the Fig. 1. It was appeared, that some hyperbolic arrays exist in planes of pairs of parameters (σ_i, τ_k) . And parameters from these arrays lead to oscillating solution of the linear approach.

In general nonlinear case it was found, that cross-coupling of the radiation defects, excitations,

etc. changes appreciable behavior of all curves only at high values of specific concentrations when C_i , $A_i \approx 1$ and does their narrower and lower. The most essential influence on all curves renders effective cross section of the radiation defects generation. In up to a threshold regime of an irradiation, the curves for C_1 , C_3 always have maximums and curves for the agents-stimulators of the reactions always have saturation (see Fig. 1). In the regime of radiation defects generation, the maximums of all curves go down and curves become very wide. It can be explained by domination of targets amortization at high doses of the beam irradiation. Comparison of numerical and analytical results with experimental data [7,10] showed that calculated parameters have reasonable values and after their corresponding correction the model gives results close to experiment in range of several order of dose magnitude.

Conclusion

The proposed model of links storage created between nanoparticles by irradiation can be used as for theoretical investigation of the crosslinkings mechanisms as for technological applications.

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